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SURVEY AND FUTURE TRENDS OF GRAPHITE TECHNOLOGY

E. J. DUNN

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AERONAUTICAL SYSTEMS DIVISION
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WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

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FOREWORD

This report was prepared by Mr. E. J. Dunn, Materials Consultant, Thomaston, Connecticut, on Air Force Contract No. AF 33(616)-6288, Intermittent Research Analysis, The Ohio State University Research Foundation, Project No. 920, Request No. ML-248. This contractual effort was initiated under Project No. 7381, "Materials Applications", Task No. 73812, "Data Collection and Correlation". The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. D. A. Shinn acting as project engineer.

The time covered for this work extended from November 1960 to April 1961.

Acknowledgement is made of the valuable assistance of the persons interviewed and of the persons who answered letters of inquiry.

ABSTRACT

The many advances during the past three years stimulated this survey of the various graphites. The various claims, properties, and processes of graphites are analyzed to assess their practicality, reliability, and reproducibility. The properties of graphite are discussed and compared to aid the decision making designers in understanding the potential of graphites with regard to missile and space applications. Emphasis is placed on the need for a closer working relationship of the designer and materials engineer in view of the belief that graphites should not be treated as a "shelf " material, but as a family of unique materials. The discussion includes likely trends in graphite development and suggestions for advanced courses of development.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings and conclusions contained herein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:



D. A. SHINN

Chief, Materials Information Branch
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Directorate of Materials & Processes

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SUMMARY

A. General Comments

Graphite technology has advanced in the last three years to the point where it is now broadly known that graphites are a family of materials whose properties can be varied widely and controllably by adjusting its degree of anisotropy. For example: pyrolytic graphite can be made one of the best heat insulators in one direction and a heat conductor at least as good as copper in the plane normal to this direction. Obviously, it is planar in nature, and most properties in these directions are strongly interrelated.

Since a degree of at least local plasticity can often be designed into a graphite for some specific applications, less deviation from conventional design approaches is required in contrast to most brittle materials.

There is a general need for closer coordination and collaboration between the decision-making designer and the materials engineer. This need becomes even more evident from studies of the newer or horizon materials. In graphites this need is particularly important since their physical properties can be varied rather widely and a change made in one property is often adverse to some other property. With such interrelation it is mandatory that the material be designed for the specific application; it is precisely here that the close-working relation between the materials man and the designer is required. The design problems are generally solved through trial and error processes since intelligent measurements with which to specify design requirements are often lacking. Material property adjustments must be made as dictated by experimental results before success can be attained where the ultimate in properties is required. This complexity precludes the treatment of graphite as a stocked item to be used indiscriminately.

New processes and a group of coordinated non-destructive tests have made and will continue to make further improvement in graphite reliability. The problem of coating graphite to prevent oxidation is now fairly well understood by some, and is on its way to solution by materials people in general.

Future trends in graphite development include the following: (1) Fabrication of ZT recrystallized or hot-worked type graphites (National Carbon Patent Grade) based on knowledge of starting materials, control of anisotropy, and consideration of specific or likely design requirements. (2) Development of graphites incorporating cloth, fibers, and felts for lighter and higher strength-to-weight ratios. (3) Production of advanced shapes in pyrolytic graphite. (4) Production of thicker sections of free-standing pyrolytic graphite. (5) Development of metallo pyrolytic graphites as possible replacements for the conventional pyrolytic graphite. (6) Improvement of dependability of graphites.

B. Recommendations

1. A continuous study should be made of the applications and experimental uses of graphites for members such as leading edges. Where the graphites are sufficiently advantageous, environmental testing should be employed.

2. The desirability and need for graphite structural members should be determined, and, if warranted, a program to develop such structural members should be implemented.
3. Support should be provided for work in the field of graphite whiskers which would explore the possibilities of whisker reinforced graphites and development of new sources of graphite "whiskers."
4. Graphites should be tailored for specific uses, and not treated as a "shelf" material.
5. The graphite designer should assist the decision-making missile engineer during the initial design stage where there is a possibility of application.
6. Designers must allow for proper adjustment of graphite properties as dictated by early trials.
7. The possibility of increasing the strength of pyrolytic graphite by lattice cross-bonding graphites as in the diamond structure should be investigated. It should be realized that the slip-system is lost in varying degrees in this approach.
8. A study of certain diborides for providing extremely high strength-to-weight ratio graphitic materials at elevated temperatures should be performed.
9. In view of the presently significant difference in properties conferred on pyrolytic graphite by the higher degree of anisotropy as compared to graphites of any other method, the continued study of the pyrolytic method by at least one highly specialized competent organization is recommended. This should be done as long as these differences remain significant, and there is hope of reduction to practice of suitable reliability considering the importance of its use, or until the method is perfected.

INTRODUCTION

The purpose of this study is to present a state-of-the-art survey of the various graphites since many advances have been made during the past three years. The various claims, properties, and processes of graphites were analyzed to assess their practicality, reliability, and reproducibility at this time or in the immediate future. Likely trends in graphite development are pointed out and suggestions for other courses of development which may not normally be followed in the course of graphite evolution are mentioned.

The properties of graphites are discussed and compared in terms of specific or representative uses. Only brief comparisons between graphites and other materials are presented and these comparisons are incidental to viewing graphites in their proper perspective. This report does not include a complete compilation of the properties of graphites or a thorough discussion of the theoretical or technological phases of graphites. Only data and technical phases which aid in understanding the potential of graphites with regard to missile and space applications in the area of Air Force responsibility are presented.

Graphites are a unique class of materials because they have high strengths, are light, and possess good strength-to-weight ratios at temperatures above 2500°F. At temperatures above 2750°F, PT (fibrous) graphite has the highest strength-to-weight ratio of any material known at the present time. The maximum strength of graphites occurs in the temperature region from 4500 to 5000°F, but at this temperature region creep must be considered if the graphite is used for longer periods of time.

One of the primary reasons for the limited use of graphite to the present time has been its unreliability. Graphite reliability has been improved by the development of new fabrication processes and with the aid of non-destructive testing. The major disadvantage associated with this material is its poor oxidation resistance. At temperatures above 800°F, graphites must be protected from oxidation by a special environment or by some other mechanism such as coating. However, they have one advantage over most of the metals because they do not become more brittle through the ordinary temperatures approaching absolute zero. Graphites, unlike true brittle materials, exhibit one crystallographic slip-system. When using this material, special design considerations must be employed as compared to conventional metals.

To supply background, a synopsis of the discussion, suggestions, applications and recommendations of the graphite survey report of 1958 is included in the Appendix.

GENERAL MANUFACTURING CONCEPTS

There are presently three practical approaches to the manufacture of graphites: the conventional method, the hot working method, and the pyrolytic method. The hot working and pyrolytic methods have been developed to the point of practicality since 1958.

Conventional Method

The conventional production method wherein a "filler" such as petroleum coke is mixed with a binder, coal tar pitch, baked and then graphitized upward of 4500°F, produces a porous, relatively low-density graphite because volatiles up to 20 times the item bulk volume evolve; this evolution creates much of the porosity in conventional graphite (obviously, some of the porosity must be continuous in nature to allow the gas to escape or the piece would be blown apart). The associated contraction "sharpens" some of the porosity and pore channels to "cracks," and effective stress concentrators which may also cause cracks due to thermal stress. Add to this phenomena, the varying heating rate, varying temperatures, etc., of the conventional Acheson resistance furnace and the difficulty is compounded. True, some appreciable improvement is made by vacuum impregnation with pitches and the like (containing more volatiles) to partially fill the pores, and is followed by regraphitizing; after several cycles of this, a starting density of, for example, 1.55 gms/cc may be raised as high as 1.90, but obviously it is impossible to reach the closed macro-pores or to fill the crack type completely since there is a shrinkage of the impregnant upon regraphitization. Because of the inherent unreproducibility, and unreliability of the product of this process as briefly discussed above, it is the writer's belief that this process should be relegated to the production of graphites for conventional uses, except, possibly, as it might be used basically as a spacer (discussed later) for a relatively low stress-carrying shape, section, or substrate. For this reason, it will not be further discussed or considered for missile graphites in this report. The means of reducing these defects and therefore yielding better reproducibility and dependability is a corporate part of the remaining two approaches.

Hot Working and Pyrolytic Methods

The hot working methods, starting with somewhat conventional or special grained materials, and the pyrolytic methods, wherein graphite shapes and plates are formed by carbon deposition with concurrent graphitization from a hydrocarbon gas at elevated temperature and controlled pressure, now appear to have been developed to practicability.

In the primary hot-working method, the pressure of working, literally squeezes out the porosity and may heal cracks as well as cause some recrystallization. This produces the ZT type graphites of National Carbon Company. There are other variations of pressure processes, for instance, pressure compacted curing wherein a resin or plastic is included in the mix which is then heated to set the resin; this may then be conventionally baked or pressure baked previous to either conventional graphitization and/or hot working. These early pressure steps will possibly convey different properties to the finished graphitized piece. They will also confer an even greater uniformity or reproducibility to it but this would be relative, and, while important, is not sufficiently so at this time to warrant discussion distinct from hot-working. However, wide variation in finished properties can be conveyed by choice of the starting "coke" for, if the crystallites in each grain of "coke" and/or the shape of each grain is such that lamellar-type or preferential compaction will result, a high degree of anisotropy will be obtained.

In the pyrolytic method, one of several gases, methane, for example, is decomposed at elevated temperatures and usually at reduced pressure, to deposit carbon (graphite) from the gas phase on to a surface as a coating, or if it is so desired, strip it, if it is sufficiently thick. It is believed that subsequent discussion will indicate that this method is basically a thin section, or coating producer, at least at this time.

Present prices should not be a determining factor in either of these two methods; both will be materially reduced, but it presently appears that pyrolytics will remain more costly per unit of weight.

AVAILABLE SIZES, DENSITIES, PROPERTIES

A brief discussion of the sizes, densities, and physical properties of graphites is given in the following paragraphs.

Sizes

The largest single pieces of conventionally made graphites are monoliths 2 ft x 10 ft x 12 1/3 ft or as large as 2 ft x 4 ft x 30 ft; the latter is made by joining several pieces together with a baked resinous adhesive. This graphite material ordinarily has a density of 1.70 gms/cc and a rupture strength of 2500 psi. Rupture strength at the baked joint is 2000 psi. Conventional graphites exist in bulk shapes but they all exhibit a variety of densities and properties. Conventional graphite rounds up to 100 inches in diameter have been produced commercially.

Hot-worked ZT graphites made by the National Carbon Company as part of the Air Force "Advanced Materials Project" are available. The ZTA graphites can be obtained in pieces 8 1/2 inches in diameter, ranging in density from 1.92 to 1.97 gm/cc. A piece this size will weigh approximately 44 pounds and the present cost is \$1100. The first piece this size cost \$6000.

Larger sizes of the hot worked ZT graphites have been made on an experimental basis. Pieces 12 to 14 inches in diameter by 10 to 12 inches long have been made by overloading the old equipment. Newly designed equipment has just been installed for making the 12 to 14 inch diameter pieces. Additional equipment for making hot worked ZT graphites of 30-inch diameter is presently on order. When fabricating the 30-inch diameter shapes a uniformly high density can probably be obtained for the whole length of this material. It is well to note that as sizes considerably larger in diameter than these become necessary, the machine capacity must be built and developed, requiring a total lead time of approximately two years.

There is no pyrolytic graphite in solid curved pieces of small diameter due to the nature of the deposition process. Pyrolytics are presently made into plates, hollow cylinders, cones, and other shapes of this type which have moderate to large radii of curvature and thicknesses up to possibly 1/2 inch. The pyrolytic type of graphite is not a bulk graphite, in the sense of the ZT types from which odd and intricate shapes may be machined without exposing inferior surfaces. There are no technological reasons known that limit the making of pyrolytics to any size. Hollow sizes up to 35 inches in diameter by 72 inches long are presently available, and equipment is on order to produce pieces of hollow pyrolytics of 48 to 72 inches in diameter by 9 to 12 feet in length which should be available by the end of 1961. The pyrolytic graphites are made in a variety of densities, but the present trend is to have the density in the area of 2.20 gms/cc.

Density

Density has lost some of its meaning since our knowledge of the graphites has increased. This is illustrated by the fact that the graphite with the highest strength-to-weight ratio has the lowest density. Also strength, oxidation rate, and other properties can vary markedly and somewhat independently of density. By means of new processes and techniques the density range has been expanded to 0.7 gms/cc (foams as low as 0.1) to 2.25 gms/cc. The theoretical density of a single crystal is 2.26 gms/cc. It has been suggested that elevated temperature irradiation could produce densities above the theoretical value but this is seriously questioned.

The fibrous and cloth reinforced (PT) graphites create the low-density graphites. The PT-like graphites are not made by the pyrolytic method because the present deposition process, when used on fibers or graphite cloth, produces a poor structure.

The improvement from hot working graphites has produced materials with densities of 2.19 gms/cc. Pyrolytic graphites with a density of 2.25 gms/cc have been made. A very thin coating of a high density pyrolytic will provide a film which is practically impervious to gas. Orientation is the major factor affecting the density of good pyrolytics; for an orientation ratio of approximately 1000/1 the density is 2.25 gms/cc, while at approximately 5/1 the density is reduced to 1.51 gms/cc.

Physical Properties

The tensile strength of graphites ranges from 1,000 to 20,000 psi at room temperature. From space temperatures to about 2200°F the strength remains practically constant, but increases at an increasing rate from 2200°F to about 4500°F through 5000°F. At approximately 4500°F the tensile strength for most graphites levels off and as the temperature increases above 4500°F the strength begins to decrease. Some graphites exhibit strengths in excess of 60,000 psi around this temperature. These very high strengths are found in those pyrolytics which have a high degree of anisotropy; a pyrolytic, having such a strength

in one plane, would exhibit a strength in the order of 1500 (fifteen hundred) psi from room temperature to 1800°F in the plane normal to that of the high strength. In the case where strength is required in all directions a more isotropic graphite such as ZT is required. A complete set of properties for a ZTA graphite is shown on table 1. Representative strengths for the ZT material would be 5000 psi at low temperatures and 10,000 psi at 4500°F.

Thermal conductivity is of importance in many applications; in general terms, if the highest conductivity is desired in one plane of direction this can be obtained coupled with the very high strengths above (in thin sections as above) provided that, in the perpendicular direction high insulating capacity and the cited low strengths are acceptable. If better perpendicular conductivities or strengths are required then the other direction properties must be sacrificed to a considerable degree as this property is extremely structure sensitive. (See Graphite General Discussion)

Conductivity characteristics are as follows:

At 1100°F * Copper = 210.0 BTU; pyrolytic graphite "ab" = 200.0, "c" = 0.3 BTU; a typical metallo pyrolytic graphite "c" = 0.05 BTU; Magnesia = 2.0 BTU/hr/ft²/°F/ft

Table 1
Properties of Special Grade of Hot Worked Graphites (ZTA)

Property	Units	Grade ZTA
Max. Grain Size	Inches	0.006
Bulk Density	g/cc	1.95
Specific Resistance	10 ⁻⁴ ohm cm	
"ab" WG (with grain)		8.0
"c" AG (across the grain)		17.5
Flexural Strength	lb/in ²	
WG		5500
AG		2900
Compressive Strength	lb/in ²	
WG		12,500
AG		13,000
Youngs Modulus	10 ⁻⁶ lb/in ²	
WG		2.40
AG		0.90
Coefficient of Thermal Expansion	10 ⁻⁶ /°C	
WG		0.8
AG		7.2
Thermal Conductivity	BTU/hr/ft ² /F/ft	
WG		85
AG		48
Admittance	cm ² /sec (He)	
WG		1.6 x 10 ⁻⁸
AG		

* This temperature is more realistic of the properties in the working range, since some properties drop appreciably from their room temperature values upon heating in the low range.

GRAPHITE GENERAL DISCUSSION

Those aspects which are common to the various families of graphites are discussed. Graphites appear complex because they have characteristics which are common to both metals and true brittle materials. They have only one slip system at temperatures below approximately 2500°F; it occurs along the basal planes and will allow quite limited cold deformation. This single slip mechanism makes it improper to class graphites as a brittle material, but since there is no slip-mechanism in the planes of other directions, graphites have many characteristics common to the brittle materials.

The important and confusing distinctions of graphites from metals and brittle materials are twofold. First, the extreme anisotropy possible with graphites cause their properties to vary with direction relative to the atomic-lattice of the single crystal. The pyrolytics more closely approach the single crystal structure and properties, which makes them very sensitive indeed to the structure. Secondly, many of the properties of graphites such as strength increases as the temperature increases thereby acting quite differently from most materials. Since graphites are of interest because of their usability over a wide range of temperatures (sub-zero to excess of 5500°F spread) these differences add to the confusion.

To illustrate the directional or anisotropic characteristics of this material, consider the following examples: the thermal expansion of a single crystal from room temperature to 1850°F is approximately 1×10^{-7} in one planar direction but 280×10^{-7} in the perpendicular direction. By special processing, it has been demonstrated on a laboratory scale that the thermal conductivity (ratio) in the single crystal approaches 10,000 times greater in one direction than in the other. This factor very markedly decreases as the temperature increases, and becomes "negligible" at 3400°F. During this wide thermal conductivity change there is little change in the electrical conductivity because electrical conductance occurs by a different mechanism type and is affected by grain boundaries while thermal conductivity is lattice vibration.

Tensile strength differences are tremendous, with graphite whiskers (a special case of single crystal) reported as 3,000,000 psi at room temperature; this represents single crystal "ab" strength (modified by a factor for small diameter). The "c" single crystal strength (physically immeasurable) would probably be several orders of magnitude less than this. This is academic, for these values are the goals for limited values. Even at this early development stage in state-of-the-art, there are pyrolytics of 20,000 psi "ab" vs 1,500 psi "c," a difference of 10 times; and, this 20,000 becomes upwards of 60,000 at 5000°F.

In a material such as this in which hardly a single property other than variability can be said to be characteristic of graphite (to make use of such extremes), an understanding of the structure is essential.

Structure

A single crystal is made up of a stack of planes or discs, similar to a deck of cards, as illustrated in figures 1 and 2. Each plane or card is composed of carbon atoms and forms a continuous series of hexagons joined together in the plane, as in the benzene ring of much organic matter. The width and length of the card are termed "a" and "b" directions, which, in the case of single crystal graphite, are equal. The thickness of the card is the "c" direction. The interplanar space, or space between the planes, is 1/2 of the

actual unit cell "c" dimension because every other plane is directly superimposed over the second plane parallel to it and not to the next plane since it is transposed. This type of arrangement creates severe anisotropy within the lattice itself. The forces holding the carbon atoms together in the plane of the ring are relatively strong, in the order of 160 kilocalories per gram atom. The weak Van der Waal forces holding the ring planes together are in the order of 4 kilocalories per gram atom. (The strength of these bonding forces is inversely related to the interplanar spacing.) Although the dimension between ring atoms is 1.45\AA , the "a" cell dimension is 2.46\AA , and the "c" cell dimension is approximately 6.7\AA (see figure 1).

Just as a deck of cards slips, graphites slip in the "c" direction of the stacked planes, thus permitting limited plasticity or deformation. This deformation is limited more in graphites than in metals because in the case of graphites, slip can occur below 2500°F in one direction only; slip in the other directions is prohibited by the ring bond forces.

Since the above concerns a single crystal of graphite, it is necessary to continue the discussion on the structure in some detail to explain the several mechanisms which cause departure from the severe anisotropy of a perfect single crystal. These mechanisms must be understood because the departures created by the mechanisms markedly affect the properties which make graphite a unique material.

A crystallite can range in dimension, in both the plane direction and stacking direction, from approximately 10\AA to thousands of \AA as in the case of natural graphite. The size of the crystallite has a definite effect on the interplanar spacing. As the size of the crystals increases the interplanar spacing decreases. The minimum layer spacing for large crystals is 3.35\AA and occurs at 15°C . In crystals whose size is less than 150\AA the layer spacing approaches a maximum limit of 3.44\AA . The density change with structure is probably inherent, and this density change should not be confused with that due to the various types of porosity of practical graphites.

Turbostratic structure exists when the layer planes are not lined up so that the atoms in the hexagon rings in every other plane are over one another as they should be. The term turbostratic is derived from the two words stratic, meaning the planes are stratified or stacked, and turbo, meaning that the alternate planes are slightly rotated or mismatched. This is one type of departure from the true periodicity form of anisotropy. The highest density graphites, the pyrolytics, result from annealing in excess of 3000°C , and are completely ordered. The turbostratic structures become well-ordered at 2200°C . The turbostratic departure from anisotropy is perhaps responsible for a minor portion of the difference in thermal conductivity between the single crystal and the pyrolytic graphites; the major portion is due to the crystallite boundaries. It is also reported that the planes can be wrinkled within a portion of the crystallite.

The graphite crystallites or crystals are much smaller than metal crystals. In metals the crystals can be seen individually under an optical microscope. The smallest graphite unit usually discernible by the microscope is the grain, which is composed of a number of crystallites. The second departure from complete anisotropy is that the crystallites within a grain can have almost any orientation to one another. They can be randomly orientated, or they can be almost all lined up with small angle boundaries, as in the case of high density pyrolytic graphites. This second departure from anisotropy partly explains why the starting materials have a definite effect on finished properties of conventional and hot-worked ZT graphites. The orientation situation for the non-pyrolytic materials is confused further by the addition of a binder to cement the grain together. This binder also carbonizes and graphitizes which introduces further orientation confusion. A material

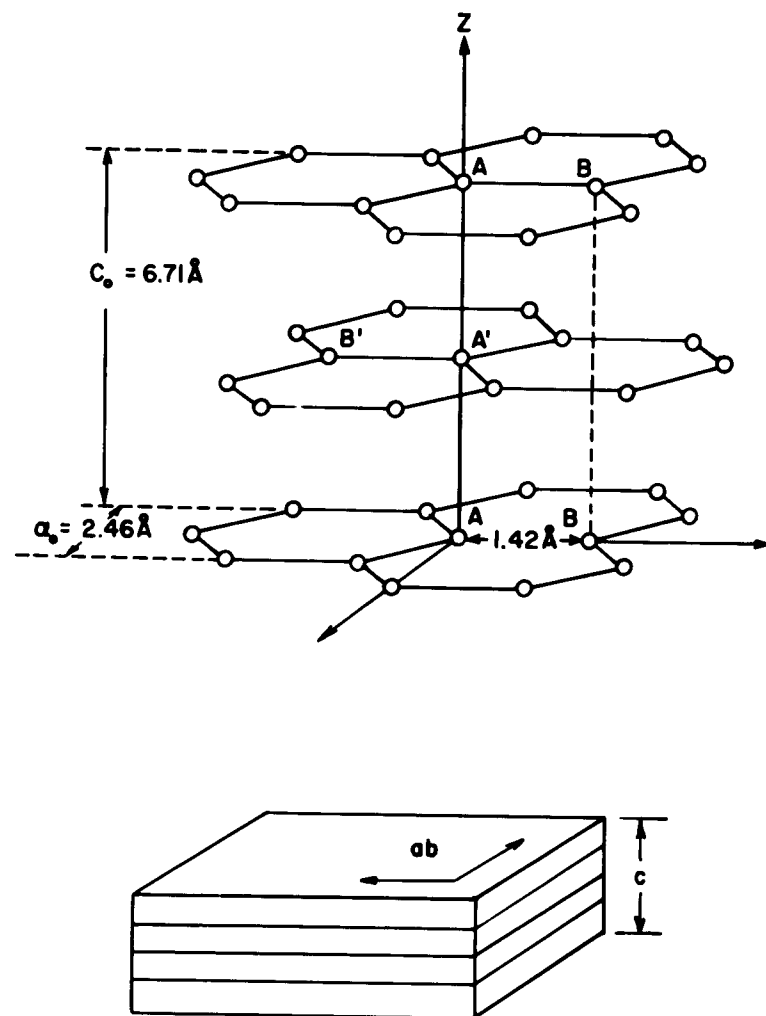


Figure 1. Graphite Lattice

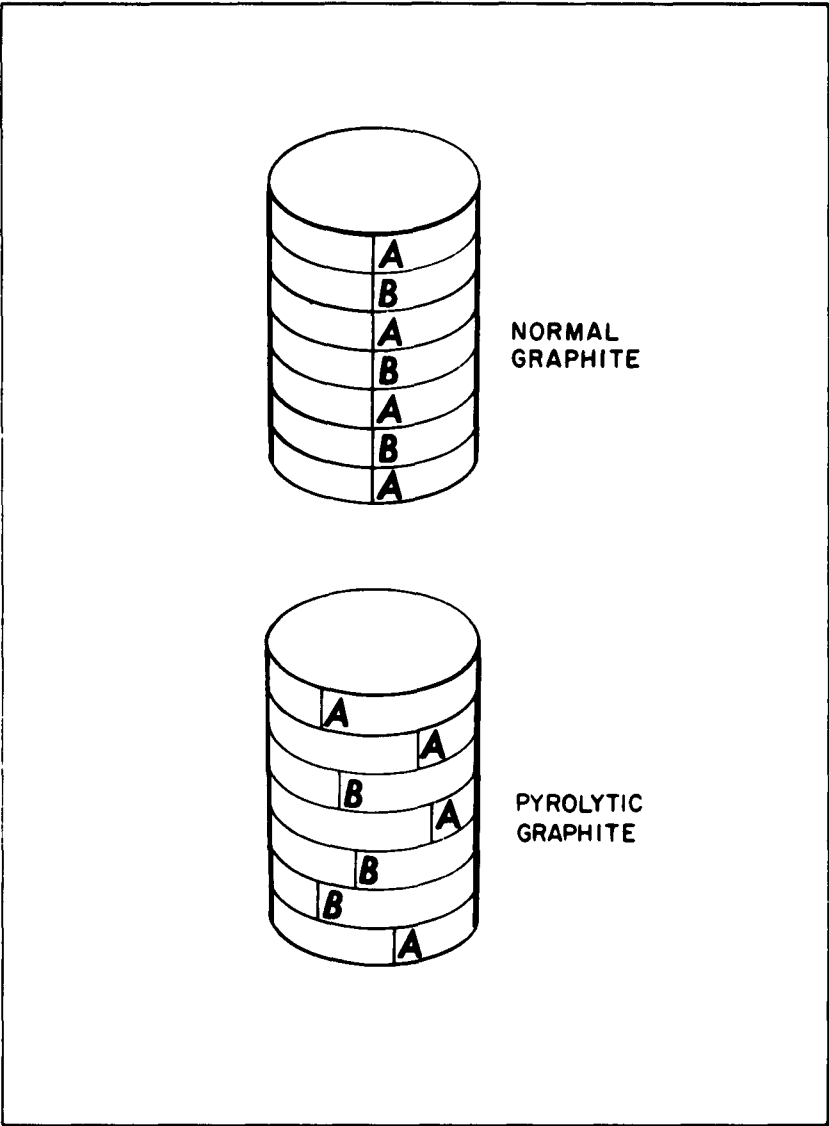


Figure 2. Representative Comparison of Normal Graphite and Pyrolytic Graphite Basal Planes

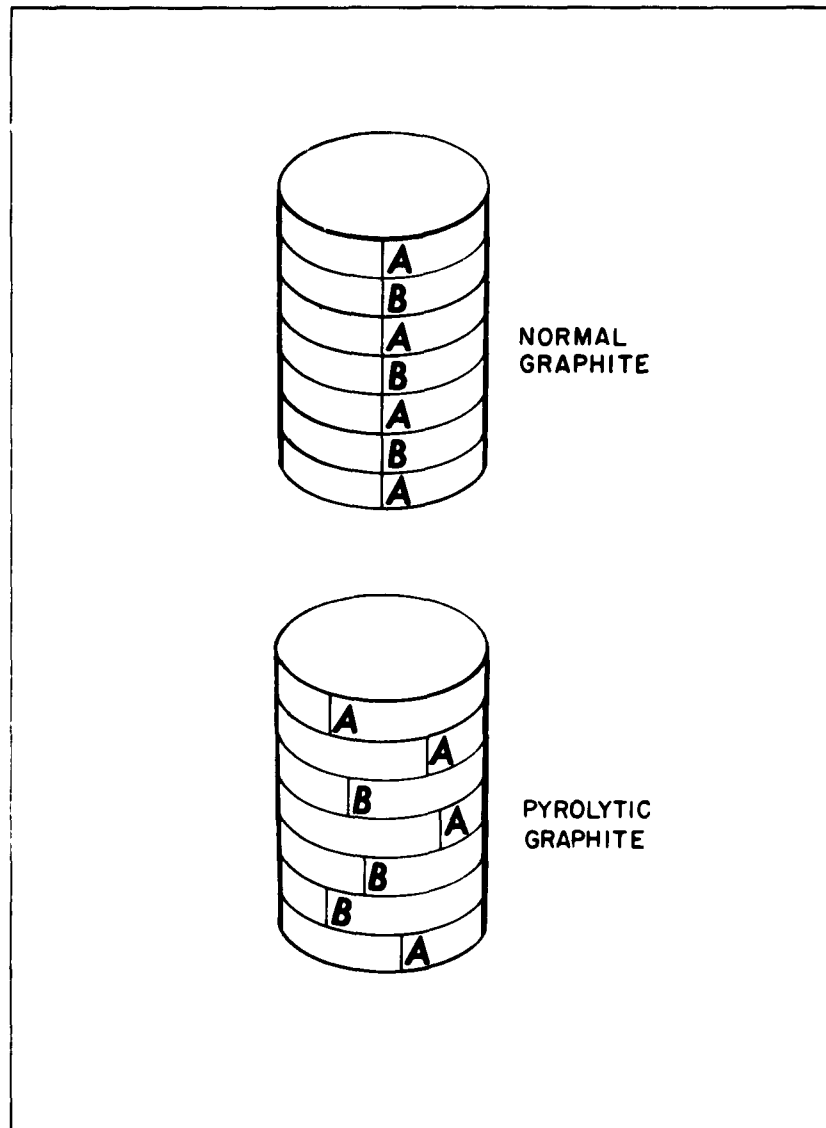


Figure 2. Representative Comparison of Normal Graphite and Pyrolytic Graphite Basal Planes

that produces coke grains composed of randomly oriented crystallites (isotropic material) could not produce an anisotropic graphite unless complete recrystallization and preferred reorientation were accomplished. This might just possibly happen under very special conditions in hot-worked ZT graphites. A highly orientated but undesirable dendritic structure can result from very high temperature hot-working.

It is possible to have grain in which most of the crystallites are preferentially oriented and have another major departure from anisotropy. The third departure would be where the grain is randomly oriented to the other two thus destroying the effect of the preferred orientation of crystallites within the grain.

The second and third type departures from anisotropy, dealing with crystallite orientation within the grain, can cause or are associated with some major decrease in density. In the case of the turbostratic departure the density change is caused by submicroscopic "porosity" or lattice imperfection. Another submicroscopic "porosity" is that associated with crystallite orientation. Submicroscopic "porosity" should not be confused with the gas evolution, shrinkage porosity, and fissures which are more prominent in the conventional graphites than in the hot-worked ones.

Anisotropy or preferred orientation can be quantitatively understood more easily with the aid of the conventional model shown in figure 3. A flat sample to be studied is placed in the center of a sphere and the orientation of each crystallite of the sample is revealed by drawing a line normal to its basal planes, and marking a point on the sphere wherever each normal penetrates the surface of the sphere. The sample normal or "pole" relates the orientation of the crystallite to that of the sample. The distribution of the many points on the sphere is described by a point density. If the sample has a preferred orientation the point density in the direction of orientation will be larger than any other; the ratio of this area density to the pole density is used as a quantitative measure of degree of preference. In pyrolytics the point of density at the pole is high as compared to the equator.

An anisotropic or completely oriented material would have a ratio approaching infinity, while an isotropic or completely random oriented material would have a ratio approaching 1. In pyrolytic graphites a 20/1 would have a density around 2.0 gm/cc; 100/1, about 2.2. The ratio of any one of several physical properties in the "ab" direction to the same property in the "c" direction is also used to express the degree of anisotropy. Near room temperature a comparison of the coefficients of thermal expansion is a good indication of degree of anisotropy. For instance an expansion ratio of 200/1 is considered a high degree of anisotropy, although the ratio of a single crystal approaches infinity, as "ab" direction expansion along the grain contracts up to approximately 750°F. It then begins to expand but remains a relatively low value compared to the expansion across the crystallite. The ratio of thermal conductivities is also used as a measure of anisotropy.

It is reported that if plots are made of tensile strength versus departure from true anisotropy for the "ab" and "c" directions, the maximum strength occurs at a point slightly removed from complete anisotropy. This indicates that some physical cross bonding, crystallites lined up approximately at 90 degrees to the major orientation direction, is required to develop maximum strength in the "ab" direction. The maximum strength is achieved at some sacrifice in the thermal properties since the maximum heat conductivity occurs in the "ab" direction and minimum in the "c" direction, and both occur at complete preferred orientation or anisotropy.

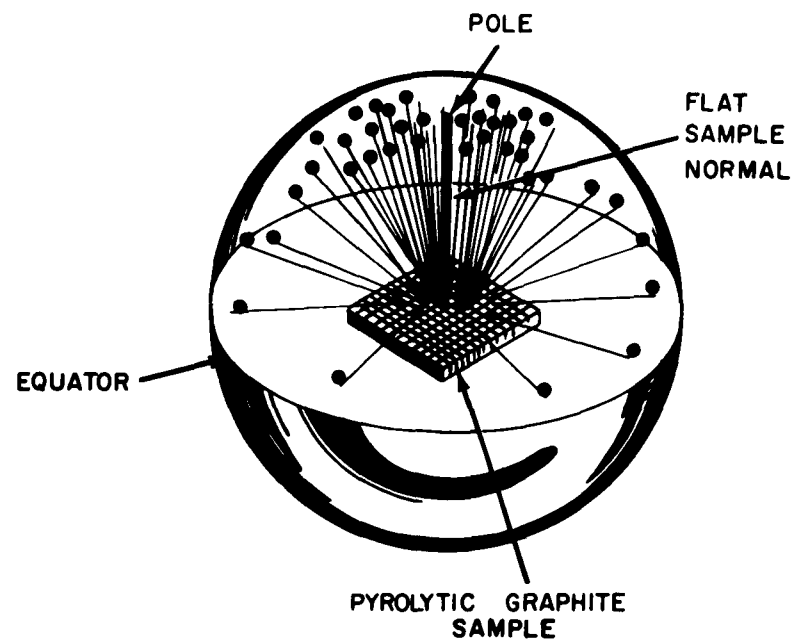


Figure 3. Pole Figure Schematically Representing Preferred Orientation

It is postulated that since the coefficient of expansion of the graphite single crystal between 32°F and 1830°F differs by a factor of 30 in the "ab" to "c" directions, a graphite that is not completely anisotropic will contain submicroscopic shrinkage "voids" and "cracks;" and, is true even if the piece were free of defects at the graphitization temperature. This postulate, although not universally accepted, explains why the strength increases markedly as the anisotropy closely approaches completeness. It, quite possibly omits the case involving turbostratic departure from anisotropy.

Indications show that some porosity is required for conventional and hot-worked ZT graphites that depart appreciably from complete anisotropy, to prevent cracking caused by severe thermal shock. The porosity may prevent some of the cracking which would occur due to the large differences in the "ab" and "c" expansions which work in random directions. This difference in expansion must have some place to go; the porosity supplies this "give". Porosity may not be necessary in full anisotropic materials, such as some of the pyrolytics. Since, for the anisotropic materials, the crystals are lined up, the expansion in a given direction is uniform throughout, and, although it varies in different directions, no cracking occurs. It is thought that turbostratic anisotropy does not effect this planar relationship.

A question arises as to whether the inherent porosity of the lower density pyrolytics (which lack the gross porosity of other graphites) is sufficient to impart high thermal shock resistance. There is a decrease in density for certain pyrolytic graphites believed to be caused by a more random orientation of its inherent lattice spread and submicroscopic porosity. At the present time the author believes that the inherent porosity for the low density pyrolytics is sufficient at least up to the deposition temperature. This view is based on the fact that voids, spaces, or porosity were created in the pyrolytics by the differential contraction in cooling down from the deposition temperature. Presently, the deposition temperature for the lower density pyrolytic graphite is approximately 3100°F. This question is of importance for if the porosity were insufficient, such pyrolytics would be ruled out for severe thermal shock applications.

It is important to note that at most temperatures, when graphite is irradiated it expands, but if it is irradiated at temperatures ranging from 600°C to 1000°C it is reported to contract, but this is open to serious question if the graphite is of near-theoretical density. It is questioned as to whether the graphites which are irradiated hot produce densities higher than the theoretical.

The increase of strength of graphites with increasing temperature is interesting because it is part of graphite's uniqueness. Like all other material the hardness and Young's modulus of single crystal graphite and similar pyrolytics decreased with increasing temperature. This similarity of properties with other materials probably means that the measured increase in strength with increase in temperature of the practical graphites is not inherent to the graphite atomic structure or lattice, but is probably caused by an increase in plasticity in the physical structure. The increase in plasticity reduces the sensitivity to notch effect of the porosity, cracks, delaminations and other defects. Further support of the plasticity theory is the decrease in density caused by the formation of cracks and pores. This type of density loss occurs in the elongated region in elevated tensile fractures when large elongations are obtained. Another way of stating the above hypothesis is that if a piece of graphite could be made free of defects, its strength would probably decrease with increase in temperature, as most other materials do, but its room temperature strength would be much greater than conventional graphite.

This hypothesis should be substantiated by other work such as determining mode of origin, and mechanism of failures in graphite structure. If full conformation were obtained it would emphasize the great desirability for elimination or prevention of notch-like porosity and cracks.

This is especially true if high strength is wanted below 2900°F, the temperature above which appreciable ductility starts to develop; and strength below this temperature must be developed if the high strengths commonly quoted for high temperatures are to be generally accepted (at low temperatures) rather than to be acceptable for only a few cases (heating with gradual load application).

The point to be emphasized is that the high temperature/high strength (and the high structural efficiency that goes with these) cannot be utilized if the member must carry the same tension load when cold as when hot; neither can it perform if the load carrying area of a member is not sufficiently hot even though other areas are. As an example, to be more specific, while graphites show a twofold strength increase, from 5000 to 10,000 psi (tension) (pyrolytics in small pieces from 20,000 to 50,000 or more) from room to 4500°F, they can't be loaded to 10,000 psi except at this higher temperature. However, if the loading can be applied gradually, and develops sufficient temperature, possible in a long slow re-entry, then the high temperature strength may be available. But, it will only be available in those areas developing sufficient temperature, and then only if the load can be decreased when the temperature decreases in the later stages of flight.

These special considerations make it desirable to mention creep at this point. Creep is an important property in the temperature range above 4000°F. The importance of creep is somewhat reduced since at these high temperatures many applications are of short duration. Below 2900°F, creep considerations can be ruled out if room temperature strengths control the loading limit. This condition will exist until room temperature strength is raised by some mechanism. One exception is where the load is increased with temperature; here again creep must be considered if the loading is high. Recorded preliminary creep tests showed the ZT materials to have a much lower creep rate in the higher temperature ranges along the grain than across the grain. The ZT along the grain creep rates were much lower than the ATJ graphite. One test, using slightly different sized specimens under a 2500 gram force at 3000°C for 15 minutes showed the deformation for ZT to equal 0.45 inch, and for ATJ equaled .173 inch.

Temperature Effect

Since most graphite properties vary greatly with temperature, an examination of its uses and properties may delineate specific temperature ranges and simplify the problem. Graphite begins to oxidize at temperatures in excess of 800°F. As a high temperature material, graphite must be protected either by a coating, its environment, or by its use where oxidation can be tolerated. When used as a material for rocket motor nozzles it is possible to maintain a non-oxidizing environment. This delineates one temperature range of 4000°F to 6000°F. For nozzle use the room temperature properties do not appear to be a controlling factor. Also in this temperature range oxidation could be tolerated in ablation use in hard re-entry.

Where coatings must be used for protection, the use of graphites may be limited to the temperature range satisfactory to the coating. Presently, for a short coating life, a silicon-rich silicon carbide coating appears most practical for use up to 2900°F. The temperature range up to 2900°F makes graphite attractive for use as leading edges and

structural members in soft re-entry. In using graphites for such purposes the low temperature properties may be the controlling factor.

At this point it would suffice to place graphites in two distinct temperature ranges. The first range is from approximately -400°F to 2900°F , and the second range is from 4000°F to 6000°F . Discussions as to temperature should be specific because the properties at these two ranges are distinctly different. There is considerable misunderstanding at present because a graphite engineer may be talking of properties based on the high range, while a designer is thinking in terms of the intermediate range. People thinking and talking in the general term of elevated temperatures are sometimes miles apart and often don't realize it.

The effect of impurities on the oxidation rate is a typical example of this confusion. Impurities definitely increase the oxidation rate up to 2900°F . Above 3200°F , impurities do not seem to have a significant effect on the oxidation rate. These temperature ranges should also be remembered in discussing thermal conductivity of graphites. The ratio of "ab" to "c" conductivities at low temperatures is in order of 100 to 300/1 for certain pyrolytics and 50/1 for certain hot-worked ZT graphites. At 4500°F the pyrolytic shows a ratio of 10/1, and the hot-worked ZT graphites are in the neighborhood of 8/1. As the temperature increased, the difference in the ratios for these particular graphites become considerably less. In some uses this small difference may be very significant. However, most of the ratio change occurs by a decrease in the conductivity along the "ab" planes and not by any large increase in the "c" direction. The insulating abilities in the "c" direction remains practically the same once above 1200°F .

From the foregoing discussion and the individual discussions to follow it is evident that the use of the word graphite in the singular is incorrect. The word steel would not be used to describe a material which has a thermal conductivity better than copper and a refractory and insulating capacity better than most refractories. In fact, the pyrolytics and the hot-worked ZT graphites are each a whole class of materials in themselves.

To give this same degree of perspective a rough comparison of some of the graphite properties at approximately 1100°F is given on table 2. The 1100°F was chosen as a representative temperature because from room temperature to about 1000°F some of the properties change quite rapidly and most steady-state uses will be at temperatures in excess of 1000°F . To give meaning to the conductivities, a typical 2.2 density pyrolytic graphite of 1/4 inch thickness, if heated to $+6000^{\circ}\text{F}$ on one side, was reported to be only in the order of 1200°F on the opposite face in 2 minutes. Such large differences in heat flow offer advantages and disadvantages in application, and are discussed later.

To complete this discussion, a brief remark on density change with irradiation is appropriate. In contrast with "low" temperature irradiation, if graphites of densities less than theoretical (2.25 gm/cc) are irradiated between $1100^{\circ}/2200^{\circ}\text{F}$, an increase in density occurs with measurable dimensional contraction. However, no increase above theoretical density has ever been observed although it is reported there is no absolute reason why this could not occur when it is noted that another form of carbon, the diamond, has a density of 3.51. Irradiation could conceivably supply the necessary energy to create a diamond-like structure at least in small local sites. However, much of the contraction effect is eliminated by a re-expansion upon annealing or heating to higher temperatures around or above 2700°F ; obviously any advantages would be lost at this temperature.

Table 2
A Comparison of Graphite Properties at Approximately 1100°F

Material	Density	Thermal Conductivity "ab" BTU/hr/ft ² /°F/ft "c"	Tensile Strength lb. per sq. inch "ab" "c"	Expansion 1x10 ⁻⁷ /°C "ab" "c"
Copper				
Magnesia		210.	5000.	
Single Crystal Graphite	2.26	800	----	1. 280.
Hot-Worked Graphite	---	150	5000.	18. 125.
Pyrolytic Graphite	2.20	170	20,000.	10. 270.
Pyrolytic Graphite	2.05	90		
Pyrolytic Graphite	<1.80	<90	1/ 40,000.	1500
Pyrolytic Graphite	1.50	not measured		
ATJ Graphite	1.73	50	1700	23. 35.
PT Graphite	0.70	<*1.2	3000. (approx)	15.
Metallo Pyrolytic Graphite		<*0.9		
Foam Graphite	---	0.5		
Whisker Graphite	*0.5		3,000,000	
Fiber Pyrolytic	---		> 200,000	
1/ Supplier estimate, brittle graphite				
* Room Temperature Value				

This problem is worthy of further study to aid in a better basic understanding in graphite, and particularly in nuclear applications. But since these effects appear meta-stable or lasting below the temperature at which graphite becomes of major interest, it is doubtful if any major advances in general graphites should be expected from such study.

TYPES OF GRAPHITES AND METALLO PYROLYTIC GRAPHITE

Hot-Worked Graphites

The process used in making the recrystallized or hot-worked ZT family of graphites inherently produces a more consistent product because it treats each individual piece in a like and reproducible manner contrasted with the conventional "many-piece-batch" method in which heating rate and time-temperature relationship varies from piece to piece; a further improvement results from the compaction during hot-working which eliminates much porosity and possibly some cracking. When working on new specially prepared filler, rather than the usual by-product coke of the oil industry even better consistency will result; since process reproducibility is more assured, the effect of the old process variables is removed from the determination of the effect of the starting materials; besides simplification, this will allow a better assessment of the effect of starting materials.

While the process itself has made major product improvement, more can be expected as more positive determination is made as to what raw material property confers what finished property. That starting materials are of practical importance to the finished product is demonstrated by the fact that petroleum cokes mixed with pitch and heated to 5400°F yield graphite; but lampblack so mixed and heated yields very little graphite structure.

For example, it is logical to expect more uniformity and more precise control of the degree of anisotropy in the end product. By proper choice and blending of raw materials it appears possible to somewhat closely approach the anisotropy and properties of the pyrolytic graphites in heavier sections, solid, and small radius-pieces which do not look encouraging in pyrolytic, at this time. However, it presently appears that there will always be some differences between the ZTs and the pyrolytics (where the pyrolytic can successfully make the piece). While these differences at high range temperature will be small, they may well be extremely significant where the ultimate is required. One such property, the heat conductivity, may be important even though it varies only from 10/1 for pyrolytic to 7 or 8/1 for ZT at 4500°F, meaning that ZT will be a poorer insulator in the "c" direction than the pyrolytic.

If "crystallite cross-bonding" were carried to the extreme so that a completely random structure occurred, then the strength would be the same in the two directions but the value would be relatively low compared to the anisotropic "ab" value; like changes would occur in most other properties (one exception to this rule would be fibrous composites). If these properties were suitable, an item could be machined from such an isotropic piece and would have obviously the same properties in any direction; but if the extreme high (or the low) values are essential to the item then it would be necessary to form (hot-work) or "deposit" (pyrolytically) the piece to shape. If the isotropic properties were suitable the item should be made from a piece of special ZT material as it probably could not be made by a pyrolytic process; if the high (or low) values are required then it could possibly

be made by either process. If absolute high or low values were required, the pyrolytic process could be required if the item geometry could be produced by that process.

A simple curve leading-edge shape could be made by either process although if an appreciable section thickness is required, the ZT method appears more practical at this time. It is very important to note that the ZT process can produce materials of a high degree of reproducibility, reliability, and uniformity. It can produce materials varying from almost uniform isotropy (and this will be improved as knowledge of individual starting material effects on end products is amassed) to those approaching the anisotropy of the pyrolytics, and this in sizes and shapes that the pyrolytics cannot presently make. It is not yet known if an isotropic material of reasonably high density can be made by the pyrolytic method, and certainly not if it can be made in bulk, or which would be required, because an isotropic material would most likely be used for items which must be machined to shape, etc.

Current ZTs are made in simple bulk shapes from which pieces are cut or machined to shape; it is to be expected and it is planned to form the simpler shapes (nose cone, cap, nozzle, and possibly, leading-edge parts) directly to shape. Doing this with a special highly anisotropic mix is expected to confer heat conductivity differences in the two directions approaching the pyrolytic values, and in the heavier section if required.

At present, ZT graphites have been made that are reported to be three fourths of the way to a complete anisotropic material.

There also does not appear to be any advantage in using pyrolytic materials unless there is a need for a high degree of anisotropy.

PT Graphites

The PT graphites are composites which incorporate graphite cloth and fibers. These presently appear to have flexural strengths in excess of 3000 psi at a density of 0.70 gms/cc.

The PTs show indications of having the highest strength-to-weight ratio of all materials, at temperature above 2750°F. A comparison of the graphites on a strength-to-weight basis is ATJ 50,000, early ZTs 80,000, and early PTs 132,000. Also important in this area are the diborides of titanium and zirconium.

Graphite cloth in epoxy resins is currently available. This is presently being used because of its good strength-to-weight ratio and good heat conductivity.

Pyrolytic Graphites

One of the most important problems of the pyrolytic producer is how to tell if the pyrolytic product is sound without destroying the item since presently pyrolytic is quite prone to delamination particularly if small radii shapes and/or increasing thicknesses are attempted. The pyrolytic producers claim that this problem has been solved by two expedients. However, the pyrolytic users have not had time to evaluate this. The two methods are: 1. A series of non-destructive tests. 2. Establishment of minimum curvature, size, and thickness limits by experience.

Testing

The non-destructive tests include dyecheck, videogauging, imagescope, and other ultrasonic and x-ray methods. These tests are presently used to guarantee the soundness in free-standing pyrolytics (pyrolytics without a substrate). It is too early for these tests to have made any significant impact on the users, but the tests should establish a basis for determining reproducibility of free standing pyrolytics if they are as good as reported. The producers' rejection rate will determine the economic practicability of such pyrolytics. However, no good non-destructive way has yet been found to determine if a satisfactory bond exists between the pyrolytic deposit and a substrate graphite or material.

This is a serious problem, particularly if the ultimate in nozzles is required because bond delamination is prevalent. One of the reasons for this is the large difference in coefficients of expansion (contraction, in this case) between substrate graphites and the pyrolytics. The pyrolytic desired for its other properties in such applications, will have a minimum "ab" coefficient (i.e., for example, 10.) which is parallel to the substrate plane whereas the substrate usually has 25/35 which is a mismatch; it is possible that special substrate graphites (which have been made, unfortunately, by the conventional method in the past) can be made by the ZT process with closer match; the "c" direction coefficient of the desired pyrolytic is approximately 280, and it appears impossible to match this in a substrate. However, if the pyrolytics are kept to thin sections this "c" match may not be as important as it is in the thickness direction of the pyrolytic; this coefficient has practically nothing to do with the change in size of a pyrolytic nozzle I.D. (only the "ab" contraction does) and it would have only a minor effect (because of section thinness) on the QD.size change (which is the I.D. of the substrate). However, if mismatch is found too serious, other expedients such as a layer of the new porous graphites can be put on the substrate before the pyrolytic, to allow some yielding.

However, the problem of non-destructively determining the integrity of this joint in either case still remains. The pyrolytic producers are trying to avoid this by promoting "free-standing" pyrolytics. The author believes this is a poor or temporary expedient, for propulsion improvement will demand higher fuel temperatures, thus bringing the problem in sharp focus again. Obviously, for the ultimate in nozzles, the best surface material plus a heat sink will be necessary at least in solid fuels, (discussed later). At any rate, a real solution to this problem is needed; and it may be easier to solve than realized because the older substrate materials were the conventional graphites whose inherent defects confused the non-destructive test picture. The use of newer more uniform graphites as substrates may well materially simplify the problem.

Presently, delamination problems limit possible thickness and curvature of pyrolytic items. One producer limits thickness itself to a 1/4-inch maximum because above this they are prone to heavy delamination; but another producer reports that a 1/2-inch thickness is now possible on larger pieces; this would be a big step forward. A year ago, even the thin sections were also delamination prone but delamination is tied up with section, shape, curvature, etc. A rule-of-thumb is gradually being established in the industry, i.e., the radius of curvature (as in a nozzle and including the throat diameter dimension) should be in the order of no less than 10 to 20 times the thickness of the pyrolytic coating. This is thought to be tied up with coefficients of expansion which are greatly different in the two directions since pyrolytics are very highly anisotropic. In a nozzle, the "c" direction is perpendicular to the curved cylindrical surface, while the "ab" direction is parallel to the curved surface if deposited to shape (It should not be machined to shape as this exposes the "c" direction laying the weak planes, both in the physical and chemical sense, open to attack).

The above rule makes it obvious that small diameter solid cylinders can't be made in pyrolytic graphite and that in hollow cylinders the smaller the diameter the thinner the allowable maximum thickness.

If the pyrolytic graphite is not to be used "free standing" but as a coating on a graphite substrate, the substrate thickness should be 10 times the coating thickness.

The foregoing discussion infers that nozzle design must be made compatible to pyrolytic requirements whereas this appears to be distinctly of lesser importance considering the ZT graphites; in other words pyrolytic graphite is less of a "shelf" material than ZT graphites for indiscriminate use as nozzle material. There have been many referrals to "mechanical cross-bonding;" by this is meant the improvement in strength etc. by mechanically fastening the layered structure together by causing some of the crystallites of the grains to be oriented at angles approaching 90° to the main anisotropic direction. In contrast to mechanical bonding, it is possible in pyrolytic deposition, to develop some diamond structure along with the usual structure. This would increase the interplanar or layer strength; it would be cross-bonding with carbon instead of with foreign atoms such as boron, etc., and would effectively fasten the stacking planes together within the crystallite. This might be looked upon as lattice or crystallographic cross-bonding. If this can be done controllably and in myriads of small areas it might well improve the "c" strength without affecting or degrading other properties including the small localized plasticity. This possibility is creditable when it is realized that the low temperature thermal conductivity is proportional to T^2 in normal graphites, to T^3 in diamond, but to $T^{2.3}$ in usual pyrolytics. This deserves further investigation.

Density

In pyrolytic graphites there appears to be a relation between density and degree of anisotropy (and properties) because the density decreases as deposition conditions are varied to cause increasing departure from complete preferred orientation. The density can be varied from approximately 1.23 to 2.25 gm/cc by regulation of these conditions. It must be remembered that high strength and high thermal conductivity in the "ab" direction (low in the "c") is always associated with high density and high degree of preferred orientation (high anisotropy). However, the crystallite size can vary and cause variation in thermal conductivity despite high preferred orientation.

When low densities are produced the orientation approaches randomness and considerable strength (and higher heat conductivity) in the "c" direction (across the grain) with, of course, a loss in strength and heat conductivity in the "ab" direction. It is to be remembered that a pyrolyte of 2.23 density is reported as preferentially ordered 1000/1, whereas one of 1.50 only 5/1. These diverging properties have pros and cons discussed under applications. The structural difference between ordinary graphites and pyrolytic types is illustrated in figure 4.

One user established a close density specification of 2.18 to 2.20 gm/cc, but found large differences in properties. These differences in properties are due to the turbostratic and crystallographic differences; obviously, density by itself is not a measure of physical properties. There are over 16 different pyrolytic microstructures, but the work required to correlate each property to a particular structure has not been done. Without Government sponsorship, it is not known when this work will be completed.

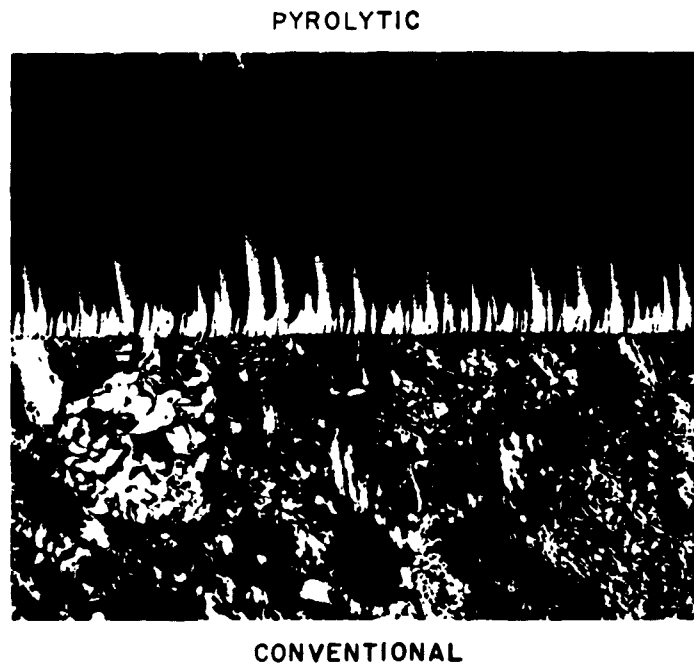


Figure 4. A Comparison of the Microstructure Between Pyrolytic and Conventional Graphites

The major decrease in density is probably due to major randomness rather than just basal randomness associated with a turbostratic structure. In other words physical or mechanical cross-bonding by crystallites, as in regular graphites, becomes more predominant with decreasing density and affects the various properties.

The lower density mechanically cross-bonded pyrolytic graphites would approach the conventional graphites in properties, except that theoretically they should have better properties because of less porosity and fewer cracks. They would be more closely comparable with the hot-worked ZT graphites. Whether the theoretical possibility can be realized consistently for the low density pyrolytic graphites is not known.

It is of paramount importance to note that pyrolytic deposition almost invariably produces a section or coating in which the graphite planes are substantially parallel to any surface on which it deposits and coats even to the point of going around corners at the substrate ends, etc. The "c" direction insulation would prevent heat from penetrating into a substrate face, but at the edges and ends the "ab" direction becomes the "c" direction of the face; high heat conduction then exists perpendicular to the face at the edges and ends. This deposition factor has major advantages and disadvantages. One advantage is that it prevents exposure of the weak plane edges at the ends of the pieces. The extremely oriented annealed pyrolytic graphites separate like mica, due to the low strength in the "c" direction. It is possible to bend this material into a 90° angle and straighten it without importing any apparent defects. This bending characteristic is similar to a cold-working operation and provides an area of considerable metallurgical interest which appears worthy of investigation. A pyrolytic graphite is presently in the market which has an unspecified orientation factor of 96 compared to the ZT graphite which has a factor of 2 on the same scale. Such radical orientation differences can cause marked differences in oxidation rate and sublimation rate.

Oxidation

One producer studied the oxidation rate of graphites at 1000°F in slow moving dry air which was free of carbon dioxide. For the pyrolytes the oxidation rate was .015 mg/cm²/min in the "ab" direction and .0375 mg/cm²/min in the "c" direction. The average value for the more isotropic hot-worked ZT graphites is approximately 6.5 mg/cm²/min. The pure spectrographic grade graphite was less oxidizable than the ZT graphite by a factor of 3 at 1000°F. A comparison at a somewhat higher temperature shows a factor of 3 in favor of the oxidation rate of pyrolytics over the conventional graphites.

Since pyrolytic graphites are made from hydrocarbon gases they are reported to be generally purer than the specially made small size spectrographic grade graphites. Most impurities increase the oxidation rate, but the rate remains constant as the impurities increase up to approximately 10 ppm (parts per million), then it abruptly increased with increasing impurity level.

The "ab" to "c" oxidation ratio in pyrolytic graphites is 3 to 1. The "average" direction oxidation rates, as determined by one laboratory, for commercial graphites as compared with dense pyrolytics is as follows: at 1100°F, commercial graphite oxidizes about 20 times as fast as dense pyrolytics; at 2200°F, 7 times as fast; at 2700°F, 5 times as fast; at 4200°F, commercial graphite oxidizes 3 times as fast as dense pyrolytics. These results are not necessarily agreed upon by other sources. Some sources have reported differences considerably less than these and still others state that the effect of impurities is cancelled out above 3200°F.

The experimentally determined oxidation rate of non-pyrolytic graphite is not truly indicative of its property degradation because the binder graphite is apparently preferentially oxidized at a faster rate than the coke particles. This is similar to intergranular corrosion in metals, in which the strength is reduced at a surprisingly high rate. In high fluid velocity flow, particles of graphite could be physically removed as the binder graphite oxidized. This phenomenon may not be important in nozzle use since reducing conditions may be maintained. Most of the conflicting results are somewhat academic because in actuality a protective coating or a non-oxidizing environment will probably be used.

Sublimation

Considerably less ablation or evaporation is reported to take place in the dense pyrolytic graphites than in the conventional graphites. For example, when pieces of conventional and pyrolytic graphites are heated at the same time in a vacuum to 5800°F, the conventional graphite lost 30 percent by weight and the pyrolytic graphite did not lose any weight. This loss in weight difference is presently thought to be due to the variation in anisotropy. Since the conventional graphite is more isotropic or randomly oriented, it exposes many more crystallites to effectively increase the area exposed, thus permitting faster ablation. The subject of ablation is very controversial, but if this evaporation difference does exist it apparently disappears at temperatures above 6150°F. In more practical terms, if the shape is such that the edges are not at a high temperature or not openly exposed but only the plane surface is exposed (as is usually the case in pyrolytic deposits since they deposit on any reasonable contour with the carbon planes parallel to the substrate surface) there should be very little evaporation below such temperatures except at grain boundaries; (which in dense pyrolytics are small-angle boundaries, almost continuous planes) and this condition should prevail until temperatures are reached where the atom's energy equals the ring bond strength of 170 k.cal. The ZT graphites would behave somewhat better than the conventional ones due to less porosity; however a highly oriented ZT type should be considerably better than conventional graphites but just how closely it could approach the pyrolytics is questionable. Table 3 indicates the general sublimation characteristics of the graphite.

Table 3

General Sublimation Characteristics of Graphite

Temperature	Vapor pressure	Equiv. altitude*
6750°F	105 atmospheres (liq.)	1550 psi
6500	760 mm	sea level
5400	10^{-1} mm	40 miles
4860	10^{-2} mm	50 "
4480	10^{-3} mm	60 "
4170	10^{-4} mm	70 "
3860	10^{-5} mm	85 "

* Altitude at which sublimation occurs at indicated temperature; or, pressure in psi required to prevent sublimation at indicated temperature.

Strength

The pyrolytic graphites should have a theoretical Young's modulus of 200,000,000 psi, but the highest value obtained to date is 13,000,000 psi. At room temperature the pyrolytics have a compressive strength of 14,000 psi when the load is applied to the plane edges (normal to the "c" direction). This is similar to a tensile stress-strain for a steel exhibiting a yield point. The compressive strength of pyrolytics when loaded on the plane surfaces normal to the "ab" direction is 68,000 psi and catastrophic failure occurs.

Metallo Pyrolytic Graphite and Pyrolytic Reliability

One producer believes that the newer metallo pyrolytic graphite materials will replace the pyrolytics. The metallo pyrolytic graphites are pyrolytic graphites that have had a carbide forming metal deposited with it, possibly creating a cross-bond. This was mentioned in the author's 1958 report (see Appendix). Boron metallo pyrolytic graphite is an outstanding example of this type of material. The latest information on this graphite showed this material to have a thermal conductivity of from 1/4 to 1/2 of the best pyrolytic graphite in the "c" (insulation) direction, and a higher strength and conductivity in the "ab" direction. This metallo pyrolytic material is reported to have demonstrated superiority over the pyrolytics when used as a nozzle in a solid propellant containing aluminum powder, producing 850 psi at 6200°F.

One producer states that they readily and easily make cones of 6-inch base diameter from boron metallo pyrolytic graphite, and that it exhibits a room temperature strength of 20,000 psi in the "ab" direction and very little creep at 30,000 psi at 4500°F. Another producer states that from a test of 500 small non-selected pieces of this graphite, the minimum room temperature rupture strength was 16,000 psi, and the maximum strength at room temperature was 30,000 psi. The most frequent of value rupture strengths found (80 to 90 pieces of the 500) was 23,000 psi. This frequency data shows the "no failure value" was 16,600 psi.

Approximately six months ago even the simple symmetric pyrolytic nozzle was extremely difficult to produce. Improvement has been quite rapid. The present reliability for these simple properly proportioned nozzles is reported to be about 90 percent. Reliability work becomes necessary as the design becomes asymmetric or complicated and new fabricating techniques are required.

It is doubtful that any of the non-destructive tested pyrolytic graphites have been delivered to the users. Whether the users realize that the tested pyrolytics can be guaranteed, probably at extra cost, remains a question. There is no use-data presently available on the non-destructive tested material.

A few experimental users were questioned concerning the reliability, reproducibility, and guaranteeable quality of the pyrolytics. Their reports were somewhat general in nature. One user received 10 to 15 pieces of a pyrolytic graphite in cylindrical form of 1 foot in diameter by 4 feet to 6 feet long. These were visually tested, but were not specifically tested and guaranteed by the producer. The user tested these cylinders by x-ray and ultrasonically found them sound. The limit of the users testing ability is not known. A few of the cylinders were also environmentally tested and found satisfactory. This same user did not receive any satisfactory pyrolytic graphite from another producer.

Since radii specifications of pyrolytic graphites has become known one user has received some nozzle components of 6-inch O.D. x 4-inch I.D. throat x 6 inches long. O.D. sizes of 8 inches are available.

The users state that considerable strides have been made in pyrolytics during the past 1 1/2 years, but results indicate that they remain non-reproducible. These results are apparently based on pyrolytic pieces which were not given the supplier's complete non-destructive tests or guaranteed satisfactory. This may also be an overlapping of material supply periods which included the time producers did not realize the scope of the design limitation.

COMPARISON OF HOT-WORKED ZT AND PYROLYTIC GRAPHITES

The present status of graphites makes it difficult to make a reliable comparison between the pyrolytics and the hot-worked ZT graphites.

The hot-worked ZT graphites may well have better performance as nozzles than the present dense pyrolytics in cases where oxidation is not a problem, and for fuels operating above 5500°F where a heat sink is desirable. The thermal conductivities of the hot-worked ZT graphites in the radial direction will be higher than the pyrolytics. The presently produced pyrolytic graphites are excellent insulators in the radial direction due to their inherent anisotropic structure. The hot-worked ZT graphites, of the approximate same density as the pyrolytics, can never quite reach the degree of anisotropy of the pyrolytics, therefore the thermal conductivity of the (hot-worked ZT graphites) will be higher than that of the pyrolytics in the "c" or radial direction and lower in the "ab" direction.

It is the opinion of the prominent industrial missile materials groups that both pyrolytic and hot-worked ZT graphites will be used for nozzles, the specific use depending on the operating conditions. They also feel that composites of pyrolytic graphite on hot-worked ZT graphites will be of great importance. Some hot-worked ZT development work for improving such composites should be encouraged. The composite graphites definitely illustrate the importance of solving the problem of determining if a good bond exists between the pyrolytic and the graphite substrate.

The pyrolytic graphites, by the nature of their properties and processes, seem ideally suited for coatings or thin sections of soft contour and large radii. This method requires extremely long periods at high temperatures in special atmosphere and expensive furnaces. The deposition rate of pyrolytics is currently in the order of .005 inch/hr, which means that it requires approximately 50 hours to deposit a 1/4-inch thickness. When the time involved in preparation, heating, cooling, and unloading the furnace is added to the deposition time, pyrolytic graphites become a slow process. The process will remain expensive unless some catalytic method can be developed to increase the deposition rate without degradation of properties. There are now definite indications that the deposition rate can be increased by a factor of 5 in the very near future. The problem of delamination in heavier sections is another factor which encourages the use of the delamination process in thin section and coatings.

Some difference in heat conductivity at 4500°F, in the order of 10/1 for pyrolytics and 8/1 for hot-worked ZT graphites, will always exist, as well as differences in other properties. The pyrolytic graphites are also interesting because of the ease and uniformity of adding elements to the graphite structure to make the newer metallo pyrolytic graphites. It is the opinion of the author that at least one competent organization whose existence

depends on successful pyrolytic should be supported to develop the pyrolytic process. The support should continue as long as the pyrolytic process remains inviting or is perfected. The reasons for this is that in certain applications where the ultimate in certain properties is required these small differences might be of extreme importance.

DISCUSSION OF GRAPHITE COATINGS

One of the main problems associated with graphite coatings for oxidation protection up to at least 2900°F is matching the coefficients of expansion between the coating and the graphite base. The differences in expansion for some of the prominent materials is shown in table 4.

Table 4

Coefficient of Expansions for
Various Graphites and Graphite Coating Materials

MATERIAL COATING	GRAPHITE	Coefficient of Expansion ($\times 10^{-6}$ in/in/°C)	
		"ab" direction	"c" direction
	Single Crystal	1	280
	Pyrolytic	10	270
	ZT	20	125
	ATJ	35	35
SiC		Approx. 45	
X C		60 to 65	
SiO ₂		50	

The coefficient of expansion for graphites depends on crystal orientation. Expansion match can easily be achieved by proper orientation control or blending of the graphites. However, if the other properties required of the graphites exclude a specific blend, then the matching can be solved by several other methods. In the case of the base graphites which have the required properties but poor expansion match, a layer of compromise expansion is deposited and then the coating; or where necessary the layer can have a graded expansion from the base expansion to the coating expansion. A layer of porous low density graphite can be deposited on the base graphites. The porous graphites provide an excellent coating surface and permit large mismatch in expansion due to their inherent pliant characteristics. Another solution is to coat and use the low density material for the complete body as it has the best flexural strength-weight ratio of any of the graphites, although later discussion shows that the use of the low density graphites tends to decrease coating life in the case of siliconizing.

Considerable work has been done on coating graphite with a silicon-rich silicon-carbide coating. One company, which has performed considerable work on this siliconizing process, feels that they have solved the oxidation problem. They believe this coating should be applied to a graphite with a specific degree of isotropy, presently thought to be 1/3, based on the expansion ratio of 280/1. By having the proper mix the expansion coefficients of silicon carbide or most any carbide could be matched so that cracking and spalling are prevented. If not sufficiently matched and if spalling does take place, it will occur in the graphite and not between the carbide layer and the graphite since the bond is sufficiently strong. This siliconizing work was performed primarily on

graphites of 1.6 to 1.8 gm/cc density, but successful coatings have been made on higher and lower densities. The nuclear AGOT (expansion 20×10^{-7}) always yields cracks in one direction.

The siliconized coating on a graphite of matching expansion so that no cracks are formed, does show excellent protection qualities. For example, a sample with a coating thickness from .003 to .004 inches which was held at 1830°F in slowly moving air from 12000 to 13000 hours showed only a slight increase in weight and no oxidation of the graphite base. The increase in weight was due to the oxidation of excess free silicon.

The durability of the siliconized graphite is sensitive to density and time-temperature relationships in the range of 2000° to 2900°F. At 2300°F the durability is stated to be 1000 hours (40 days), but at 2500°F the durability is reduced to a few days. If the graphite density is relatively high the durability at 2500°F is believed to be 1000 hours or more. Graphites having greater than average porosity are believed to allow the free silicon to migrate faster from the coating into the graphite thus leaving a permeable silicon carbide coating. Since the migration is probably a diffusion effect, it probably takes about 500 hours at 2500°F to reach the permeability at which oxidation of the base graphite starts.

The siliconized coating on graphite nozzles showed no measurable throat erosion after testing for 2 minutes in a 800 psi liquid propellant at 5500° to 5800°F. The solid propellants are believed to remove the free silicon, but even when this reaction doesn't occur, there is no erosion improvement over the uncoated graphites.

There is no known limit as to the size of graphite which can be coated, other than the equipment. Presently solid or tube shapes approximately 4 1/2 inches in diameter by 8 feet long can be coated. The recommended thickness for the silicon carbide coating is .005 to .008 inches. Laboratory scale samples of a pyrolytic coating on a graphite substrate have been successfully coated.

The reason that graphites are used for the base material instead of a silicon carbide containing free silicon is that graphite is easier to make. The graphites are much easier to machine and therefore cheaper than the carbides. Silicon carbide in heavy sections is sometimes regarded as being more prone to thermal shock than graphites.

Another graphite company is credited with having a very superior coating, one which would repress the volatility of graphite and allow its use up to temperatures in excess of 7000°F, but no substantiation of this coating could be obtained. A heat-treated graphite, called AHD, being made, was stated as having a density of 1.95 to 2.0 gm/cc, at least on the surface. A missile company, using the AHD graphite, states that the AHD reliability is much better than conventional graphite and believes it solves their problem, but not to the exclusion of other graphites. Other graphites are still being considered by this user.

When considering the use of graphites for re-entry materials the useful temperature range depends upon many variables. Two important considerations for graphites are the time-temperature relation of coating life, and also if the graphite item is to be reuseable. If the coated item is to be reused, the coating's temperature and that of the underlying graphite must remain sufficiently low to prevent failure during service life. Some modifications may be necessary to allow for thermal-stress situations developed in the coating from temperature cycling caused by reuse.

The time-temperature data on siliconized graphite provides information for determining the usefulness of this material. For instance, at 2500°F, with no modification for recycling stresses, the effective coating life appears to be on the order of 500 to 1000 hours. The coating life also depends upon the porosity of the underlying graphite. Since it was mentioned earlier that a porous graphite could exist next to the coating, some figure below 500 hours coating life should be considered for 2500°F operation and considerably less time at 2900°F.

Caution should be observed when using graphites with coatings. Most coatings are brittle but strong. The coating may crack under load if the base material's Young's modulus is too low with respect to the coating modulus under an efficient load. Cracking occurs because for a given applied load, the base material stretches more than the brittle coating material. In the case of silicon carbide with free silicon, the modulus is in the order of $60 \text{ to } 70 \times 10^6 \text{ psi}$, while for graphites the modulus is $3 \text{ to } 15 \times 10^6 \text{ psi}$. This is an appreciable discrepancy in the modulus values, but in some applications the temperature/loading relation may change this picture.

There are several ways of eliminating the modulus discrepancy trouble. An undesirable cure would be to limit the load. Three other methods include the following:

1. The development of graphites of higher modulus.
2. The use of a porous graphite interlayer with sufficient pliancy to accomodate the mismatch in moduli. This may be required in order to accommodate the mismatch in expansion anyway.
3. The development of coatings of closely matching moduli.

The use of the porous graphite interlayer looks most promising as an immediate solution but there is a possibility of developing graphites of higher modulus when it is noted that graphite whiskers have a modulus in the order of $100 \times 10^6 \text{ psi}$.

APPLICATIONS AND PROPERTIES OF GRAPHITES

Rocket and Missile Propulsion Units

In the rocket and missile propulsion field the use of graphites with solid fuels is particularly interesting. However, graphites were used for jet vanes in liquid fuel propulsion units during 1958 and possibly earlier. A detailed discussion of jet vane used with liquid propellants can be found in the Appendix.

Since maximum erosion resistance at temperatures in the range of 5400°F and higher is desired for uses such as exit cones, entrance caps, and nozzles for missiles using solid fuel propellants, graphites are thought to be a feasible material for these. At operating temperatures in the range of 5400°F, room temperature properties do not appear significant as long as the material has sufficient thermal shock ability. To prevent oxidation of the graphite at these high temperatures, a reducing environment is desirable, but slight uniform oxidation is sometimes allowable.

The high density pyrolytics are advocated by some for nozzles. Those advocating pyrolytic graphite tend to suggest the free-standing type of material in an attempt to bypass the problem of satisfactory bonding to a substrate. The oxidation and volatilization

is minimized in this anisotropic material because only the ring plane surfaces are exposed. The oxidation and evaporation rate from the plane surfaces are believed to be considerably less than from the edges at least up to 6150°F. This type of graphite provides one of the best insulators known through the wall of the nozzle. They may be satisfactory for solid fuel temperatures up to 6100°F for short durations. To increase the allowable exposure time at temperatures in the neighborhood of 6000°F the surrounding pressure must be raised since the vapor pressure of the graphite is appreciable: 10^{-1} mm at 5400°F; 1 atm at 6500°F. Rocket motor pressures are elevated which might explain why graphite works with such high temperature fuels.

However, as temperature and exposure time requirements increase, the nozzle surface temperature must be prevented from increasing; the thermal conductivity in the diametric direction must be improved to remove the heat from the inner surface. In a discussion of this with one pyrolytic graphite producer an idea developed which would make the nozzle a composite with stacked annular rings or washers (plates) of pyrolytic graphite. The "ab" direction would be the diameter (thereby having high diametric heat conduction in this portion) machined to the proper I.D. contour, and deposited upon this inner contour, the pyrolytic material normal to the ring pyrolytic material thereby obtaining the usual advantages at the nozzle surface but supplying heat removal of the remaining heat coming through into a high conductivity high capacity sink; or the inner surface could be a free standing nozzle bonded to the rings by a separate graphitization. But serious expansion problems may occur here. In either case, it appears that to lower the inner surface temperature any appreciable degree, the inner pyrolytic graphites "c" conductivity must be materially improved and adjusted possibly for each specific set of conditions. It would be ideal if this could be done without lowering the "ab" conductivity but this is unlikely. This whole solution would require much work and perhaps should be regarded as conjectural at this stage because of the many problems that can be foreseen (not including some unforeseen problems that undoubtedly will arise).

It may be found more practical to use a thermally and expansion-controlled pyrolytic graphite deposit on a like-adjusted ZT substrate. If too much adjustment is required it appears desirable to use a second approach as the nozzle tests on even the present early ZTs are reported at least comparable to the best pyrolytics and more reliable at this time, i.e., develop the most anisotropic ZT or, in other words, make one to approach the "c" conductivity of the pyrolytic and use that ZT by itself. In the previous case the "c" conductivity of the pyrolytic graphite was to be improved, by moving it in the direction of the present ZTs.

To make larger items up to 10 feet in size, the pyrolytic manufacturers suggest a free-standing pyrolytic graphite section backed up by some other material like fiberglass laminate. For the ultimate in fuels, this type of composite still has the problem of an inside surface temperature that is too high for long exposures at high temperatures. It would be possible to lower the inside surface temperature by developing a cross-bonded pyrolytic which would, incidentally, also have a slightly lower density. This method would improve the "c" (diametric) conductivity but lower the conductivity in the "ab" (length) direction. Besides affecting the thermal conductivity in the "ab" direction, the cross-bonded pyrolytic graphite would reduce the strength and possibly reduce the thermal shock capacity. The thermal shock would probably be affected since the only appreciable porosity present in a good pyrolytic would be the small size and limited amount created by the contraction in cooling from the deposition temperature. There would be none of the larger kind associated with other types of graphites. Yet the operating temperature, being higher than that of deposition, would seem to demand more space (porosity) to create the "give" or pliancy to accomodate this increased expansion and

that which is due to the increased temperature of those areas further removed from the inner surface, which will be more quickly at a higher temperature due to improved heat flow. This would become more serious with increasing size. This consideration might even preclude the manufacture of cross-bonded pyrolytics (those departing appreciably from anisotropy) in thicker sections. This expansion requirement for porosity would probably decrease as the pyrolytic approaches complete anisotropy and possibly disappear near crystallite alignment.

There appears to be a maximum density, at least in both commercial and recrystallized graphites, where the highest thermal shock capability is obtained. For example, a hot-worked ZT graphite of 2.05 gm/cc density may crack, but by lowering the density slightly the cracking may be eliminated. A different starting material, recrystallized graphite, can be hot-worked to the 2.05 gm/cc density and will not crack, but its tensile strength will be lowered due to the change in anisotropy.

Graphite cloth in epoxy resins are currently receiving attention for use in blast tubes. These graphite cloths in epoxy resins have better strength-to-weight ratios than fiber-glass epoxy, and they are also better heat conductors. Crude burn-through tests show the graphite epoxy a better heat conductor than the glassed epoxy.

Re-entry

The kinetic energy of a satellite re-entry from space is reported as approximately 13,000 BTU per pound of vehicle at 17,000 mph and at least 27,000 BTU per pound around 25,000 mph. The temperature developed on a re-entry supporting surface or member is primarily dependent upon the rate of deceleration, heat dissipation, and location in the re-entering structure.

For space-craft non-exact atmosphere re-entry injection, a large degree of maneuverability is essential if a landing is to be made at a specific earth location; this involves relatively long periods at elevated temperatures, the exact time and temperature depending in part on craft "density" and the rate of deceleration. "Hot structure" designs may be essential for the heavy vehicle, longer re-entry periods; and structural graphite, yet to be developed but now recognized (first suggested in 1958 report, see appendix; now mentioned in 1961 MAB Report 169-M), will probably prove to provide the most efficient material. This is particularly true for leading edge surfaces and immediate substructure surfaces, and may later be proved true for deeper structures from comparison of materials on a yield strength-to-weight vs temperature basis, particularly if the common-temperature strength can be improved. The final comparison may also involve creep, so perhaps the comparison should be on a creep strength-to-weight basis. Dynamic-creep may possibly need consideration, although it appears that if room temperature strength limits must be used, as is now the case, creep can be ignored.

According to a leading edge study, generally acknowledged as the first realistic approach to design in brittle materials, graphite pieces 6 inches in diameter by 6 inches long min. (preferred 10/12 inch diameter x 24 inches long) are required; sizes considerably larger than this are no problem to fabricate. This comparison showed that graphite is superior in the order of 8 1/2 pounds per unit to 12/13 pounds in moly (approximately 30 percent weight saving) and this is based on ATJ graphite; when the newer hot-worked materials are considered with twice the ATJ strengths, and with many times more reliability there would appear to be no question of graphite superiority. This application should be restudied using the far superior realistic values of ZT graphite, the likely values for high-strength low-density graphites now emerging (for their "surface give")

should aid in the anti-oxidizing coating problem, and there localized crushability without crack propagation should require less departure from conventional design). It must be noted that molybdenum also requires an oxidation-preventing coating. If any of the graphites prove to be as highly advantageous as now appears likely, more impetus and fully environmental testing should be given. With a few experiments to point the way, a graphitic material can be developed and produced to do the job.

There are other variations on graphitic bodies to be included in this study. For example, it has been suggested that the metallo pyrolytic graphite deposited on a suitably shaped substrate of graphite (if properly adjusted thermal expansion or expansion compensated) would be an ideal leading edge for such items as the Dynasoar. It has also been suggested that a varying pyrolytic body be deposited on a wing contour (which could be a permanent graphite substrate, for attachment strength, of the proper expansion coefficient) varying from a highly oriented pyrolytic (for its "c" insulating value) of sufficient thickness to one capped off by a siliconized coating for oxidation prevention on the outer surface. It is also very possible that low density PT material (.70 gms/cc) will be brought to the producible stage with a flexural strength of 3000/3500 psi. This looks very interesting from the leading edge standpoint where a coating for protection is required since the material will not only have a very high strength-to-weight ratio, but a good bonding surface for coating adhesion (mechanical), porosity for high thermal shock resistance and to allow "give" to accommodate thermal expansion difference between the basic graphite and most coating materials (which ordinarily causes the usual flaking); porosity will also contribute to its low thermal conductivity or insulating ability.

POSSIBILITIES AND RECOMMENDATIONS FOR GRAPHITES, INCLUDING STRUCTURAL USE

The structural possibilities of graphites which were suggested prior to 1958 are mentioned in the Appendix. The recommendations listed below also suggest the greatly improved structural possibilities of the newer graphite techniques. A discussion of a very general nature is provided to give some details involved with the specific recommendations.

1. As each generation of applicable graphites is developed a study should be pursued to a logical conclusion concerning its characteristics as a design material. These study programs should be flexible so that sizeable increases and decreases in the rate of work could easily be made by a suitable steering group. There are some materials presently ready for the preliminary studies leading to a major work rate in a few months. It is significant that the unreliability factor and the coating problem connected with past graphites have been solved to an appreciable degree.

2. The desirability and need for graphite structural members as compared to other materials should be determined. If the graphites are desirable, a program to develop the structural members should be implemented. Such determinations would require periodic coordinated advice from the most competent non-conventional design and graphite materials engineers. There are many variations of graphites which could possibly bring to fruition successful beams and other structural members. Some of these variations are discussed on following page.

A standardized regular grade of graphite substrate covered overall, but particularly on the moment of inertia areas, with a 1/4 inch highly anisotropic pyrolytic material may be used. The pyrolytic deposit will support high tensile and compressive bending stresses from some temperature, for example -300° to 2900°F and higher (2900°F limit imposed by present coating limitations). It may be necessary to put an expansivity adjusting coating between the pyrolytic and the siliconized coating and also between the pyrolytic and the substrate shape if thermal expansivities cannot be adjusted without seriously compromising other desired properties. Where substrate failure appears possible, the new graphite cloth reinforced PT graphites could be used as the shape material. The PT graphites have the best strength-to-weight ratio of any material known at such temperatures. In this type of application the low temperature strength may be the design control value.

In the scheme of graphite technology the first generation of graphites may be the Acheson process type graphite, including impregnation. The second generation of materials would be the hot-worked graphites and the pyrolytics. The third generation might be the oriented starting materials applied to the hot worked graphites, and metal additions in the pyrolytics. The fourth generation could be fibrous structures and composites particularly in the low-density high-strength range, and further extension of metallo pyrolytic graphite systems. The fifth generation could be the whisker reinforced graphites. The whisker graphites are not of interest to the tonnage graphite consumers and hence will get scant support from industry.

The term "whiskers" is used only in the case of certain special fiber-like graphites. These whiskers are of super strength, three million psi or more, and presently reported to be grown only by one graphite producer. They are grown in a graphite electrode in an arc pressurized to approximately 90 atmospheres. The graphite whiskers are of more practical interest than metal whiskers primarily because they are considerably easier to grow. The whiskers are relatively simple to extract from the boule. Extraction is accomplished by thermally etching the boule at 900° to 1100°F in a flowing stream of oxygen and catching the whiskers by a screen located downstream. A pyrolytic graphite producer has noticed that in making pyrolytics a type of fiber sometimes grows in profusion, and these fibers are not in a boule. The present thought is that they may be of the same relative strength as the pressure grown boule whiskers because they have the same scroll appearance. The strength of these fiber graphites are well over 200,000 psi, but mechanical tests for determining a more accurate strength value of them have not been planned. Those involved with this type of whisker or fiber believe that investigation of the deposition conditions will reveal that they can be grown in profusion. Some work should be performed to determine if these have the same strengths as the whiskers or if they have strengths which are consistently over 200,000 psi. Even if they are only over 200,000 psi, a serious effort should still be made to delineate the maximum growth and growth rate conditions, because the possibility of practical production is encouraging. A practical use will probably be found for them even if the fibers do not have as phenomenal properties as the true whiskers.

While it is not definitely known, there are indications that the ratio of the Modulus of Elasticity divided by Poisson's ratio of the "whiskers" and of the base graphites may not be large. One of the reported reasons for the success of fiberglass plastics is that this ratio is large; this means that as a load is applied to the plastic it tends to squeeze ever more tightly to the glass fibers and this is why the load is believed to be transmitted to this smooth surfaced glass fiber. However, as stated, this ratio is not definitely known in graphites, and it is not impossible that considerable latitude for adjustment may exist in the base graphite; further, there is question whether the graphite "whisker" is as

smooth as glass, and it probably is not, then there is the question whether this criterion is valid at all. Furthermore, glass and plastics are quite dissimilar and formed at low temperatures whereas the very high temperature at which the base graphite (containing the "whiskers") must be formed would encourage the formation of bonding mechanisms.

3. It is too early to be definite one way or the other, but graphite "whisker" reinforced graphite (even pyrolytically deposited on them) is so potentially important that the cost of establishing the possibility one way or the other looks quite minor and rewards for Government needs, tremendous! It should be encouraged and supported.

Graphite technology has now reached the point where in contrast to many brittle materials, graphite, by control of anisotropy, allows a measure of ductility to be designed into the material at ambient temperatures; this will require less departure from normal design consideration but at a sacrifice of some part of the extreme anisotropic properties available (i.e., in lowering the particle anisotropy to confer slight room temperature ductility, some of the remarkable insulating capacity in one direction and heat conductivity in the other direction, may have to be sacrificed). If such a sacrifice is prohibitive then brittle design concepts must be used.

4. Graphites, because of their limited ductility by controlled anisotropy, should be tailormade and not treated as a shelf item.

5. The graphite designer should assist the decision making missile designer during the early stages of development. A very close liaison and cooperation must be developed between the user and the supplier.

6. The necessity for adjustment of properties as the result of experimentation and retrieval should be considered. The first attempts will probably isolate important parameters or indicate feasibility.

7. The possibility of increasing the strength of pyrolytics by developing some diamond structure to crystallographically cross-bond the layer planes should be investigated. It should be realized that much of the slip-system may be lost in this approach.

8. Titanium and zirconium diborides have very high strength-to-weight ratios at elevated temperatures. The plain diborides oxidizes above 2000°F, but when sufficient molybdenum disilicide is added to the diborides the oxidation temperature rises to approximately 4000°F. A study of certain diborides for providing extremely high strength-to-weight ratio materials at elevated temperatures should be conducted.

9. The pyrolytic method deserves continued adequate support because some difference will always exist between the hot-worked graphites and the pyrolytics. Metallic elements can be added easily and uniformly to the pyrolytics making them more appealing for development. A continued study on the pyrolytic should be conducted by at least one competent exclusive organization.

APPENDIX

Synopsis of Discussion, General and Specific Suggestions and Applications of 1958 Survey

To provide background which might aid in understanding the scope of the recommendations made in this present survey of graphite problems and applications, there is included in this appendix pertinent sections and abstracts of the author's unpublished 1958 report for the Department of Defense. The order of presentation from that report does not necessarily indicate order of importance.

1. Develop and investigate new missile-grade graphites which are presently to be made by special control and selection from present premium grades; later from raw materials specially selected or processed and controlled for yet-to-be-developed missile grades; remotely, from new fabrication processes and/or raw materials made by new processes.

2. There should be created a well-coordinated program to establish adequate correlation between destructive and non-destructive properties and tests of graphite on the one hand, with end use results in military applications on the other; this should have eventual specifications for selected material from present grades and for yet-to-be-developed mixes or grades as the target; this should include empirical attempts to establish indexes for thermal shock resistance, erosion resistance, etc.

3. Accelerate and complete the investigation of the effect of making graphites from petroleum coke specially produced from special crude oil "cuts" (as contrasted with the presently used, widely varying oil refinery refuse petroleum coke); desirable results to be fed into no. 2 and subsequently standardized with establishment of specifications and procedures (if necessary) to produce exact cokes to be used to produce specific missile-grade graphites.

4. Investigate the application of pressure baking process to missile-grade graphites (such baking tends to produce higher density which is desirable for some uses).

5. Investigate improvement of density and strength in general, by new mixes with and without no. 4., without undue regard to effect on thermal shock resistance for use in those nozzles seemingly not critically affected by this property.

6. Coordinate and encourage work on coatings, gaseous deposits and diffusions, impregnations, etc., to improve erosion and/or oxidation resistance of present graphites. Include such means as liquid exudation, surface cooling and protection by gas evolution, and the many other possibilities.

7. Investigate advantages of extrusion and molding to shape where these forming methods would be practical. Some producers believe there is a definite property advantage in molding or extruding because a surface film is formed.

8. Coordinate a program for filling existing gaps in property information at various temperature ranges concerning available graphites.

9. Investigate graphites of 20,000 psi or greater compressive strength with the purpose of improving the thermal shock resistance. Incidentally, the compressive strength of graphite changes negligibly with strain rate at room temperature up to 35,000 in./in./min. One graphite producer feels that shock resistance can be substantially improved without

lowering the strength materially. Since industry has no demand for such a graphite, the graphite producer would want support to explore this.

10. Develop mixes with additives to improve erosion and oxidation resistance by such means as liquid exudation and gas evolution. The erosion resistance work might include vapor deposition of hafnium carbide and tantalum carbide or compounds of these on graphites.

11. Develop and apply differential heat flow graphites.

12. Develop and investigate carbons containing reinforcing materials for use in cooler sections such as high temperature resistant wires. It is of interest to note that baked carbons are much stronger and reputed to be more erosion resistant than graphite but considerably less thermal-shock resistant. The baked carbons have been reported to fail as a nozzle material. The properties between baked carbon (fired at 1000°C) and graphite (fired to 2200°C or over) represent a gradual transition from one to the other with increasing firing temperature. The baked carbons are not used or produced on a commercial basis.

13. Consider determining indexes for thermal shock and other graphite properties by a theoretical or empirical approach.

*14. Determine the starting point of failure in graphite and its mode of progression both at room and high temperatures. Graphite is mainly composed of particles which consist of numerous crystallites of graphitized petroleum coke usually referred to as the filler material. The filler is held together by graphitized residue of coal-tar pitch, called the binder. The question is just where does each type of failure occur. It is believed by some graphite producers that at least ambient failure occurs in the pitch binder residue. It is not known whether failure occurs within the binder or at the binder-coke particle interface or even if failure starts at this point. If failure occurs at the interface, improvement in the adhesion of binder to filler should be developed. If failure occurs within the binder, a stronger type binder should be developed.

*15. Develop methods for controlling shape, size, type, and amount of porosity in graphites.

Much porosity present in graphite is generally a jagged angular type or essentially a stress concentrator which could possibly cause low strength failure. One method of increasing the strength without decreasing the porosity which apparently confers thermal shock capability, may be to control the shape and size of the major portion of this porosity. This could possibly be done by starting with a synthetic carbon or coke flour with practically no major porosity, combining with this a suitable low volatile binder and/or pressure baking the carbon, but incorporate into the starting material tiny spherical beads of a decomposable material before baking and graphitizing. The basic idea is not only to control porosity but also its shape to reduce stress concentrators and thereby increase strength without affecting the contraction and expansion qualities associated with porosity. Reduction of stress concentrators may even permit the same thermal shock resistance at a decreased porosity and hence provide better erosion resistance.

* Writer is responsible for the suggestion.

The ATJ graphites, presently limited to sizes such as 7 inches x 20 inches x 24 inches or 8 inches x 118 inches x 48 inches, have wide deviations in properties. One company believes that the properties can be controlled within much higher limits by use of pressure baking. Work on porosity size-control has probably already been started by the prominent graphite producers.

*16. Investigate methods of controlling anisotropy of cast graphites. Some work on melting graphite under pressure and casting to form a massive graphite of near theoretical density (2.25 gm/cc) has been performed for the Air Force.

An interesting fact here is that graphite has a triple point or point at which gas, liquid and solid coexist. This point is approximately at 105 atmospheres of pressure and 4000°K. At lower pressure conditions than at the triple point, graphite vaporizes directly or sublimates, and above this point graphite melts like any other solid. Hence it can be melted and cast under sufficient pressure. A cast type of graphite is generally a completely oriented columnar structure with very poor properties in one direction. Theoretically it should be possible to control the crystallizing orientation. This control of crystallizing orientation may be studied by inoculation of the melt by solid crystallite additions as well as by other methods.

*17. If graphite can be melted and cast, particularly with some degree of random orientation the question of whether or not it could be hot-worked remains. Some basic work on this problem may be worthy of investigating. However, since porosity appears to be necessary and desirable for thermal shock resistance in the conventional and hot-worked graphites, it is doubtful if too much valuable data would be derived from this investigation because this process would produce dense graphites; but, by crushing the cast graphites, the particles remaining may be used to make porosity graphites of controlled shape and size.

*18. Since the graphite structure has high bond energy within the graphite ring plane but very weak (van der Waal) forces holding the planes together it may be worthwhile to investigate the bonding of planes by use of forming elements such as silicon and other carbide.

19. Investigate the effect of catalytic impurities on oxidation rate.

20. A need exists for developing metallographic and petrographic techniques applied to the study of graphite microstructure.

21. Graphite whiskers have been produced with tensile strengths up to 3 million psi. Means of improved production of these for basic research work as well as for possible use in making massive graphite "felts" or for incorporation as reinforcing material for more conventional graphites should be investigated. This may also allow for increased room temperature tensile strength. This coupled with oxidation preventives may establish graphite as a real constructional material for high temperature use.

* Writer is responsible for the suggestion.

Specific Applications

1. Nozzles

One experienced nozzle user never found a thermal shock failure with ATJ and NT graphites. This does not necessarily indicate that cracks never developed, but since the nozzle was in compression it did not fail. At one set of firing conditions the nozzles erode excessively, but they do so uniformly and symmetrically. This type of erosion failure indicates a high degree of uniformity within the graphite. These people stated that density in the 1.5 gm/cc range yields positive erosion while densities of 1.75 gm/cc yield 40 percent less erosion and with densities up to 1.8 gm/cc no thermal shock failure occurred.

2. Jet-Vanes

As jet vane use with liquid propellants, probably no one has had more experience than Chrysler-ABMA group and it is essential to detail this. This group has seen thermal shock failures in graphite so used when the density goes above that for sound CS 312 (an extruded grade) approximately 1.60, and this without deflecting the vanes; in static full-scale tests the vanes have never been used to deflect the missile exhaust despite the fact that this is what they must do in practice, because present test facilities do not allow deflection (*this of course prevents compounding thermal shock with the transverse load which must be borne in use; it illustrates the difficulties experienced with materials, and in this case may have lead to overspecifying, if such has occurred.) All molded grades except one GBW has failed mostly by fissure cracking in the direction of exhaust flow with subsequent rapid scouring erosion of the open crack; but all of these passed their specialized collimated x-ray tests with flying colors, a test which does separate the good and bad in CS 312 (extruded); the one molded grade that does work, does not do so consistently, and the good and bad cannot be distinguished by any of their non-destructive tests including the x-ray; while those that work give 3 to 5 percent less erosion than CS 312. The loss of inspection control far outweighs the erosion improvement. (*It is suspected that theoretically if the x-ray could be applied in the other direction, defects that make the difference may appear; the x-rays must pass at right angles to the pressure flow used in forming the graphite and this is difficult in this case for the increased thickness in this direction, approximately a factor of 3, makes this impractical, possibly obscuring the defects). Chrysler favors using room temperature flexural strength plus their specialized x-ray technique as an indicator of suitability; they use their x-ray not only for crack, void, fissure, and low density area or volume detection within a given piece, but as a constant technique standardization, also for density comparison from piece to piece, grade to grade etc. They reject 80 percent of the graphite they pay for. However, their problem is economic. At the present 120/160 sec. firing time, they have a material that works; it is expensive but certainly not prohibitively so. They are very careful, but they must be when it is remembered that the loss of a sizable portion of just one of the four jet vanes means the loss of the missile.

Comment

(*) The jet-vane results indicate a most important fact; jet-vanes require a certain combination of strength, density, and thermal shock resistance; the problem is to balance erosion (strength and high density) versus thermal shock resistance (structure plus porosity give-and-take); high strength properties coupled with high density generally gives better erosion resistance but lower thermal shock resistance (i.e., 312 works; ATJ doesn't) (these factors weigh differently in the case of a nozzle which is kept in compression whereas vanes are not). These facts point out that there will be no all-purpose

graphite grade but rather one for each type of job or major use parameter; that porosity is essential to the higher apparent or compression-free thermal shock resistance required for vanes or possibly other extreme heating rates; and that the graphite structure is not inherently sufficiently shock resistant for such rates. Obviously, higher density is not the encompassing panacea it first appears; neither is the quest for new production methods leading to higher density; however, they certainly are worth pursuing for uniformity.

One research group states, "very high density graphites available here and abroad have been disappointing in physical strength, thermal shock resistance, gas erosion and control of anisotropy. (*Besides the anisotropy which may be suspected of causing low directional strength, the lack of porosity may likewise have caused poor shock resistance, fundamental methods of producing high density graphite to be used as raw materials for subsequent assembly, discussed elsewhere herein, into massive usable graphites should still be sought diligently; perhaps this assembly including controlled size and shaped porosity should be regarded as a new concept).

In manufacturing graphite, petroleum coke is mechanically mixed with warm coal-tar pitch; a balling action occurs, the product from the mixer, grading from a quite noticeable amount of balls (size-peas, marbles) to a mix almost exclusively of balls. Traces to discrete balls quite often can be detected in the finished graphite piece persisting through the extrusion or molding and firing processes. Groups of small balls create areas of low density, and even if compaction is sufficient to give a uniform density, true bonding does not always occur at the ball-mix interface resulting in included weak surfaces. High relative movement of material in extrusion or molding is necessary to obviate these; better control and more adequate processing is required.

A means to protect graphite from high temperature oxidation at least for usable periods of time is very important. This is substantiated by the fact that graphite is the only material with an appreciable tensile strength at 5000°F. With possible improvements in properties as the result of accomplishing some of the work listed in the suggestions, graphite should become more inviting.

Another point of interest in graphite technology is the size factor. The problems from research to practice and hence to usable size graphites are tremendous. Actual usable sizes should be familiar to at least all those who use graphites so that any disillusionment will be prevented.

There had been some talk within the industry to install press equipment for producing sizes over 40 inches in diameter. A survey at this time produced no support from the users for such sizes.

* Writer is responsible for the suggestion.

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<p>Mr. E. J. Dunn, Materials Consultant, Thomaston, Connecticut, SURVEY AND FUTURE TRENDS OF GRAPHITE TECHNOLOGY, by E. J. Dunn, February 1962. 44 p. incl. figures & tables. (Project 7381; Task 73812) (ASD TR 61-353) Contract AF 33(616)-6288. Unclassified report.</p> <p>A survey of the various graphites, in view of their advances during the past three years is presented. The various claims, properties and processes of graphites are analyzed to assess their practicality, reliability, and reproducibility. The properties of graphite</p> <p>(over)</p>	<p>UNCLASSIFIED</p> <p>1. Graphites 2. High Temp. Materials 3. Ceramic Coatings 1. Proj. 7381 Task 73812 II. Contract AF33(616)-6288 III. Dunn, E. J. IV. Not avail. fr. OTS V. In ASTIA collection.</p>	<p>Mr. E. J. Dunn, Materials Consultant, Thomaston, Connecticut, SURVEY AND FUTURE TRENDS OF GRAPHITE TECHNOLOGY, by E. J. Dunn, February 1962. 44 p. incl. figures & tables. (Project 7381; Task 73812) (ASD TR 61-353) Contract AF 33(616)-6288. Unclassified report.</p> <p>A survey of the various graphites, in view of their advances during the past three years is presented. The various claims, properties and processes of graphites are analyzed to assess their practicality, reliability, and reproducibility. The properties of graphite</p> <p>(over)</p>	<p>UNCLASSIFIED</p> <p>1. Graphites 2. High Temp. Materials 3. Ceramic Coatings 1. Proj. 7381 Task 73812 II. Contract AF33(616)-6288 III. Dunn, E. J. IV. Not avail. fr. OTS V. In ASTIA collection.</p>	<p>UNCLASSIFIED</p> <p>discussed and compared to aid the decision making designers in understanding the potential of graphites with regard to missile and space applications. Emphasis is placed on the need for more co-operation between the designer and materials engineer in view of the belief that graphites should not be treated as a "shelf" material, but as a family of unique materials. Likely trends in graphite development are pointed out and suggestions for advanced courses of development are mentioned.</p>	<p>UNCLASSIFIED</p>
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